Rectifying properties of magnetite-based Schottky diode and the effects of magnetic field

Y. Z. Chen, J. R. Sun,[a] Y. W. Xie, D. J. Wang, W. M. Lu, S. Liang, and B. G. Shen
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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Rectifying properties, with and without magnetic field, of a high quality $Fe_3O_4/SrTiO_3$:Nb Schottky diode have been experimentally studied. The junction exhibits an excellent rectifying behavior both below and above the Verwey temperature (T_V) of Fe_3O_4. Magnetic field has a weak but visible effect on the transport process of the junction, producing a negative magnetoresistance for $T<T_V$ and a positive magnetoresistance for $T>T_V$. Based on an analysis of the current-voltage characteristics, the spin polarization of Fe_3O_4 has been deduced. It is a strong function of temperature, varying between −78% and 18%. © *2007 American Institute of Physics*.
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Highly spin polarized ferromagnetic oxides, especially half-metallic ferromagnets, have attracted tremendous attention since the discovery of giant magnetoresistance (MR), tunneling MR, and colossal MR.[1–5] Among the half-metallic ferromagnets, Fe_3O_4 is of particular interest because of its fascinating intrinsic features. One of the most important features is the Verwey transition at $T_V \approx 125$ K, which is expected to cause a considerable change in the electronic structure of Fe_3O_4. As a consequence of the Verwey transition, a resistivity jump by two orders of magnitude and a significant magnetization drop have been observed.[6] As far as the spin polarization is concerned, though band-structure calculations predicted a −100% spin polarization,[7,8] experimental data dispersed in a wide range, and sometimes contradicting results appeared. For example, spin-resolved photoelectron spectroscopy declared a spin polarization ranging from 16% to −80%,[9–12] while negative spin polarization was scarcely detected by transport measurements.[13]

Recently, Ziese *et al.* proven that the information on the spin polarization of Fe_3O_4 could be extracted from the current-voltage (*I-U*) characteristics of the $Fe_3O_4/SrTiO_3$:Nb junction, and found that it was a positive value, ~60%.[14] Although this result is also different from the theoretical prediction, this method is quite simple and completely different from those previously used. However, we noticed that a four-probe geometry was used by Ziese *et al.* for the measurements of the *I-U* relations. As is well known, this technique is based on the assumption that the Fe_3O_4 film is equipotential. This may not be exactly true considering the high resistivity of Fe_3O_4, especially at low temperatures. Furthermore, the leakage current of the Schottky junction of Ziese *et al.* is large, which may disturb the analyses of the experimental data. Based on these considerations, we revisited this problem with the two-probe technique being used. Different from the results previously reported, the $Fe_3O_4/SrTiO_3$:Nb junction exhibits an excellent rectifying behavior both below and above T_V. The spin polarization of Fe_3O_4, deduced from the *I-U* relation with and without magnetic field, is a strong function of temperature, varying between −78% and 18%.

The Fe_3O_4-based Schottky junction was fabricated through depositing a Fe_3O_4 film on a (001) $SrTiO_3$ substrate doped by 0.8 wt % Nb (STON) by the pulsed laser ablation technique. During the deposition, the substrate temperature and O_2 pressure were kept at ~480 °C and $\sim 5\times 10^{-6}$ torr, respectively. The film thickness was ~80 nm, controlled by deposition time.

The epitaxial growth of the magnetite film was confirmed by the x-ray diffraction analysis. Transport and magnetic measurements were performed on a quantum design superconducting quantum interference device magnetometer. The junction area was 1×1 mm^2, patterned by the conventional photolithography and chemical etching technique. For the measurements of the *I-U* characteristics, two copper electrodes, one on Fe_3O_4 and the other on STON, were deposited. The electric contact was Ohmic with a contacting resistance less than 10 Ω at room temperature.

The magnetic and transporting behaviors of the Fe_3O_4 film are similar to those reported by Ogale *et al.*,[15] with the Verwey transition occurring at ~110 K. The *I-U* curves of the junction measured under different temperatures are shown in Fig. 1(a), with the temperature intervals of 30 and 20 K above and below 120 K, respectively. The junction exhibits an excellent rectifying property, as demonstrated by the strong asymmetry of the *I-U* relations against the polarity of electric bias. A similar feature is observed in the whole temperature range concerned, both below and above T_V, and the only difference is the considerable expansion of the *I-U* curves along the *U* axis as the temperature decreases. These results are different from the previous report that rectifying behavior only appeared below T_V.[14] Further analyses reveal that the *I-U* relations can be well described by

$$I = I_s\left[\exp\left(\frac{eU}{nK_BT}\right) - 1\right], \quad (1)$$

which is clear from Fig. 1(b) that shows a linear relation between $\ln I$ and eU/k_BT when $eU \gg k_BT$, where $I_s \propto T^2 \exp(-e\Phi_B/k_BT)$ is the reverse saturation current, k_B the Boltzmann constant, Φ_B the height of the Schottky barrier,

[a]Author to whom correspondence should be addressed; electronic mail: jrsun@g203.iphy.ac.cn

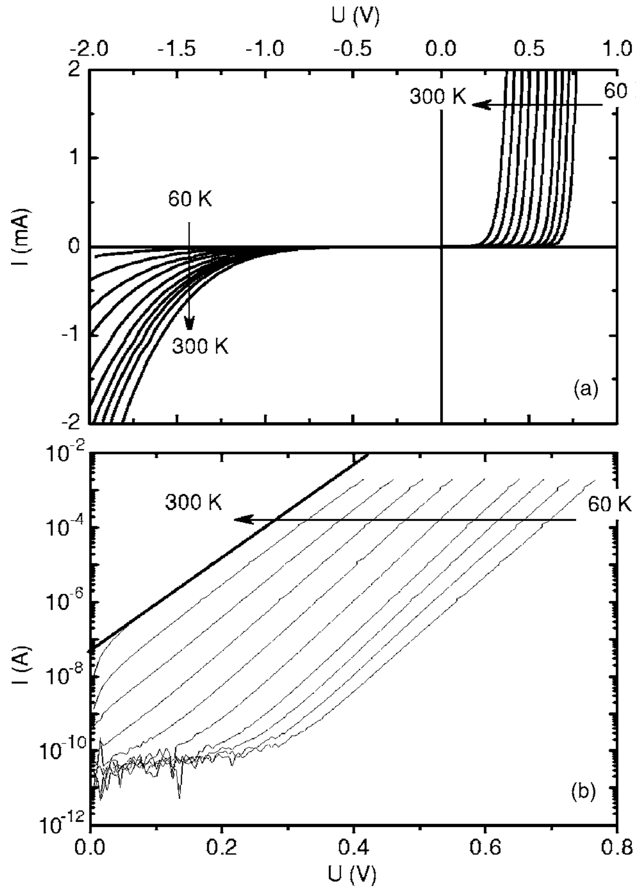

FIG. 1. Current-voltage (*I-U*) curves at different temperatures without magnetic field (a) and the corresponding semilog plot of the *I-U* curves (b). The solid line is a guide for the eye.

and n the ideality factor of the junction. The deviation from linearity is that the current is too low in the low T and low U range to be detected by our amperometer. It is interesting that the $\ln I$-U slope shows an obvious dependence on temperature, increasing with the increase of temperature below T_V while decreasing above T_V (Fig. 2). This result indicates that the charge ordering of Fe_3O_4 indeed has an effect on the rectifying behavior of the junction. The ideality factor n of the junction, derived from Fig. 1 based on Eq. (1), is also shown in Fig. 2. It exhibits a monotonic increase with the decrease of temperature, varying from 1.33 for $T=300$ K to 5.41 for $T=60$ K. The significant deviation of n from unity

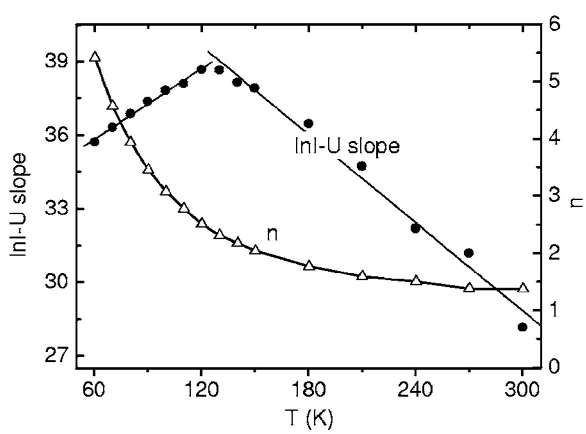

FIG. 2. $\ln I$-U slope and ideality factor n of the $Fe_3O_4/SrTiO_3$:Nb junction as a function of temperature. The solid lines are guides for the eye.

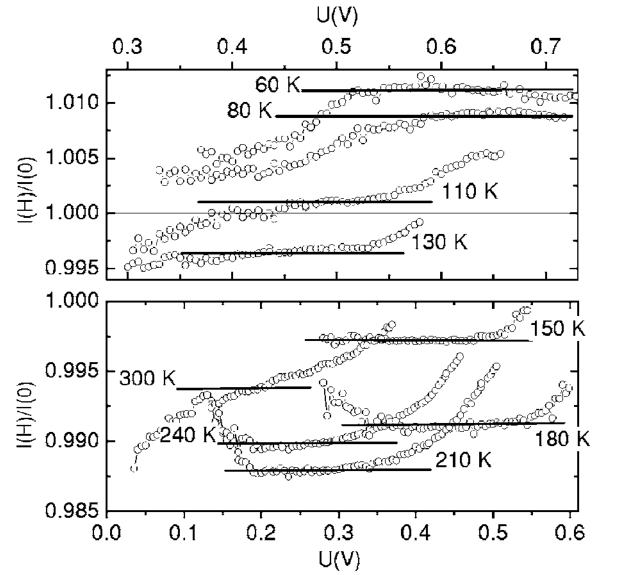

FIG. 3. $I(H)/I(0)$ ratio as a function of electric bias measured under different temperatures ($H=5$ T). The solid lines are guides for the eye.

in the low temperature range could be a consequence of the presence of considerable tunneling or leakage current. The height of the Schottky barrier, deduced from the experimental data based on the equation $\ln(I_s/T^2) \propto -e\Phi_B/k_BT$, is $\sim$0.51 eV near the room temperature, similar to that of the Fe_3O_4/GaAs diode.[16]

The effect of magnetic field is further studied. Although it is weak, the variation of the *I-U* relations under magnetic field is visible. Figure 3 shows the $I(H)/I(0)$ ratio as a function of electric bias measured at various temperatures ($H=5$ T). It is obvious that $I(H)/I(0)$ is nearly a constant in the temperature range from 60 to 240 K over a broad bias range. In the low electric bias range, effect of the magnetic field on the *I-U* relation becomes complex. In this case, the thermal current could be negligibly small because of the small eU/k_BT and the current across the junction is mainly tunneling or leakage current. These could be the reason for the deviation of the $I(H)/I(0)$ ratio from unity.

It is interesting that $I(H)/I(0)>1$ for $T<T_V$ and $I(H)/I(0)<1$ for $T>T_V$. This result indicates a negative to positive crossover of the MR as the temperature passes through T_V, which is different from the previous report that the MR remains negative irrespective of temperature.[14] The MR of the junction may arise from the Zeeman effect due to the spin dependence of the Schottky barrier, as suggested by Ziese *et al.*[14] According to Ziese *et al.*,

$$\frac{I(H)}{I(0)} = 1 + P\frac{\mu_B H}{k_B T}, \tag{2}$$

where $I(H)$ and $I(0)$ are currents across the junction with and without applied field, respectively. $\mu_B H$ is the Zeeman energy, $P=\tanh(\Delta_{ex}/2k_BT)$ is the spin polarization without external magnetic field, and Δ_{ex} the exchange energy. P is positive if $\Delta_{ex}>0$, corresponding to a majority spin parallel to the bulk magnetization. According to Eq. (2), $I(H)/I(0)$ will be independent of electric bias when the temperature and magnetic field are given. This is in good agreement with the experimental results in Fig. 3. The variation of $I(H)/I(0)$ with electric bias for $T>240$ K may be an indication for the presence of significant tunneling or leakage current.

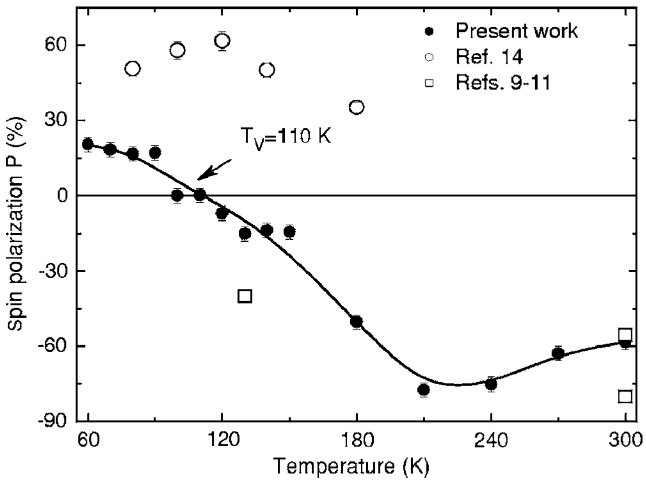

FIG. 4. Spin polarization of Fe_3O_4 as a function of temperature. Results of other authors are also presented for comparison.

From the data shown in Fig. 3, the spin polarization of Fe_3O_4 can be obtained based on Eq. (2), and the corresponding results are shown in Fig. 4. Data obtained by other authors are also presented for comparison. It shows that P is $\sim$18%, a positive polarization, at the temperatures well below T_V. With the increase of temperature, P decreases progressively and undergoes a positive to negative crossover as the temperature passes through T_V. The most striking observation is the strong temperature dependence of P above T_V. P decreases from −20% for $T=150$ K to −78% for $T=210$ K. Further increase in temperature leads to a slight upturn of P, and a spin polarization of −58% is obtained at 300 K.

In the temperature range above T_V, according to theoretical calculations, there is a band gap near the Fermi level for spin-up electrons in Fe_3O_4, and only the spin-down electron states are available. This actually implies a −100% polarization above T_V.[7,8] With this in mind, the deduced negative spin polarization of −78% is rather inspiring. This result is also in good agreement with the spin-resolved spectroscopy analysis, which gave a spin polarization of −80% for the Fe_3O_4 (111) film near the room temperature.[9] The positive spin polarization of 18% for $T<T_V$ is close to 16%, a result obtained by the study of spin-resolved photoemission spectroscopy for an oxygen deficient Fe_3O_4 surface.[12] Spin polarization in the low temperature range is an interesting issue considering the fact that the Verwey transition could affect the band structure of Fe_3O_4. It has been proven that a band gap opens near the Fermi level for both the spin-up and spin-down states below T_V.[17] The present work indicates that the spin polarization of Fe_3O_4 undergoes a negative-to-positive crossover when the compound is cooled below T_V. The positive polarization is consistent with that obtained by Ziese *et al.*, though the value is somewhat different.

Considering the lattice mismatch between Fe_3O_4 and $SrTiO_3$, interfacial defects are inevitable, a direct consequence of which may be the broadening of the Verwey transition of the Fe_3O_4 film. It is obvious that the information obtained by the analysis of the *I-U* relations comes mainly from the interface. For $T<T_V$, the bulk Fe_3O_4 behaves as an insulator due to the charge ordering. However, interfacial effects may keep the system from a complete charge ordering. Meanwhile, the presence of lattice distortions or defects such as ion or anion vacancies could affect the density of state near the Fermi level. All these make the system deviate from the theoretical expectation. This may explain the appearance of finite spin polarization for $T<T_V$.

For $T>T_V$, the depression of the charge ordering to the spin-down states disappears. As a result, the spin polarization becomes negative, approaching the value predicted by the theory. It is possible that the density of spin-up states is finite near the Fermi level in our Fe_3O_4 film, though it could be small, especially near the interface. This explains the gradual variation of P with the increase of temperature.

In summary, the rectifying properties, with and without magnetic field, of a high quality $Fe_3O_4/SrTiO_3$:Nb Schottky diode have been experimentally studied. The junction exhibits excellent rectifying behaviors both below and above the Verwey temperature of Fe_3O_4. Magnetic field has a weak but visible effect on the transport process of the junction, producing a negative MR for $T<T_V$ and a positive MR for $T>T_V$. Based on an analysis of the current-voltage characteristics, the spin polarization of Fe_3O_4 has been deduced. It is a strong function of temperature, varying between −78% and 18%.

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